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MECHANICAL PROPERTIES OF CROSSLINKED POLYMER COATINGS

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Prerequisite knowledge: Some familiarity with polymers and polymer structures would be beneficial, although not required. Also, students familiar with basic mechanical properties and their measurement for metals, especially hardness and fracture toughness, will be able to apply that knowledge to the material presented here.

Objectives

- Fabricate and test thin films to explore relations between a polymer's structure and its mechanical properties.
- Expose students to testing methods for hardness and impact energy that are simple to perform and which have results that are easy to comprehend.
- Show importance of polymer properties in materials that students frequently encounter.
- Illustrate a system which displays a tradeoff between strength and impact resistance, the combination of which would need to be optimized for a particular application.
- Expose students to coatings technology and testing.

Equipment and Supplies

- 2-mm diameter pencil leads and lead holders, to cover a range of hardnesses. The available pencil hardness range is 6B (softest) to 9H. To test the materials described here, pencils from 2B to 5H (2B, B, HB, F, H, 2H, 3H, 4H, 5H) should be sufficient.
- Steel test panels—7.5 x 15 cm, 0.8 mm thick, with dull matte finish (from Q-Panel Co., Cleveland Ohio).
- Drawdown bar (film applicator)—see Appendix.
- Micrometer.
- Drop weight impact tester—see Appendix .
- Oven(s), capable of temperature control in the range 70-190 °C.
- Large glass plate, or other hard flat surface.
- Raw materials: see Procedure for specific examples and suppliers.
- Tukon[®] or other microhardness tester (optional).

INTRODUCTION

Organic coatings, the paints and finishes we use for protection and decoration, are polymeric materials—they consist of high molecular weight chain-like molecules, which contain many atoms linked together by covalent bonds. Although the characteristics of a particular paint or finish can be modified somewhat by additives, the basic chemical and molecular structure of the polymer (or polymers) from which a coating is made is primarily responsible for many of its important properties, such as hardness, durability, and chemical resistance.

Many common coatings are composed of polymers with a crosslinked molecular structure. After application as a liquid, these finishes do not merely 'dry' in the conventional sense. They form hard solid films by undergoing a chemical reaction, called crosslinking (or "curing"), after they have been applied to a surface.

Crosslinking is a process by which linear polymer chains ("primary chains") are joined together at common junction points. These junction points can be provided by low molecular weight compounds, which can chemically attach themselves to the ends of at least three different primary chains (see Figure 1). Such compounds are referred to as "crosslinking agents" because they provide the means of converting a collection of linear molecules into a crosslinked polymer. The structure of a crosslinked polymer can be depicted a net (Figure 1), and these materials are often referred to as network polymers.

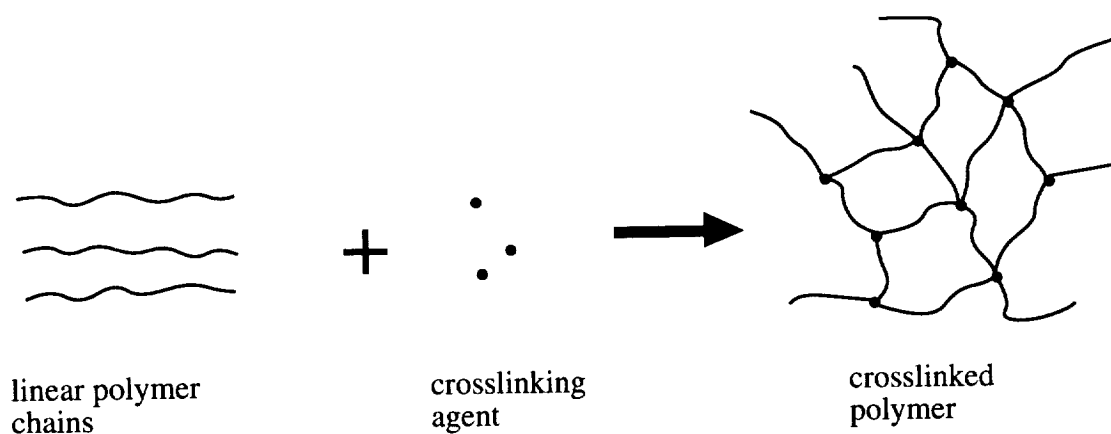


Figure 1. Formation of a Crosslinked Polymer

The properties of a network polymer depend strongly on its degree of crosslinking. To use the net analogy, a network with extensive crosslinking (many junction points, or many chains emanating from each one) would be classified as a "tight" network, while one with more limited crosslinking would be called a "loose" network. A higher degree of crosslinking in a polymer coating (tighter network) usually leads to increased hardness and solvent resistance, but may also result in increased brittleness. Other mechanical and chemical properties can be affected as well, and usually an optimum degree of crosslinking is sought which gives an attractive combination of properties for a particular application.

In this laboratory, you will prepare a series of crosslinked coatings, and will determine how the degree of crosslinking in these materials affects their hardness and impact resistance.

Like the schematic of Figure 1, you will fabricate crosslinked polymer networks by combining a primary resin with a crosslinking agent. (The word "resin" is used to describe a polymeric, or high molecular weight, compound). The primary resin consists of linear polymer chains which contain hydroxyl groups (-OH) at the chain ends (see Figure 2). Acrylic and polyester resins of this type are commonly used for automobile finishes and industrial coatings. The hydroxyl groups are the reactive sites at which these primary chains will attach to the crosslinking agent.

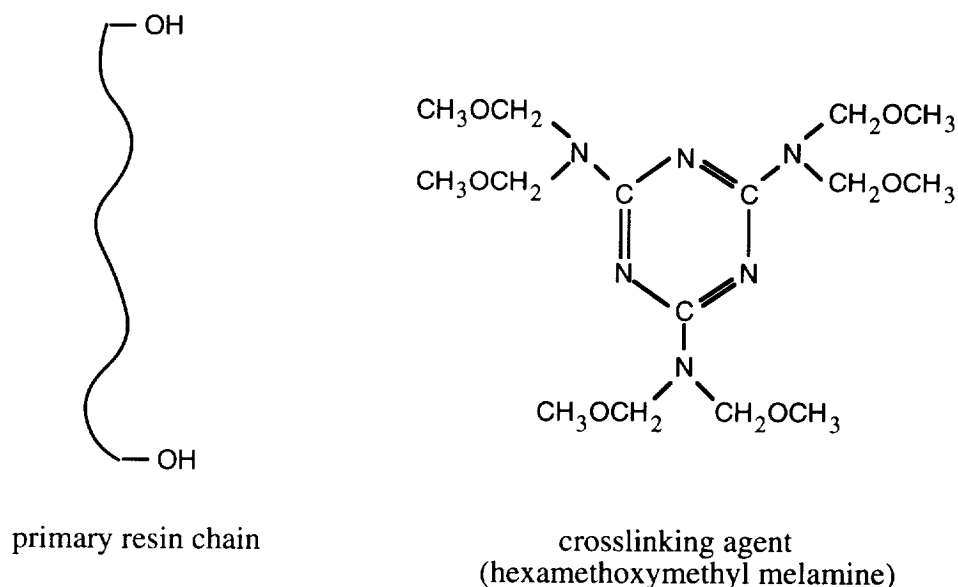
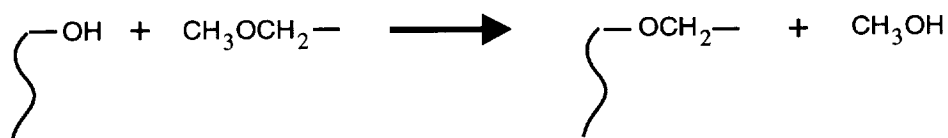


Figure 2. Components for Polymer Network

Several different types of compounds can serve as crosslinking agents for the primary chains. The one you will use is a substance called hexamethoxymethyl melamine (HMMM). Its chemical structure is shown in Figure 2.

The HMMM chemical structure may appear complex, but the important thing to note is that it contains six (CH₃OCH₂-) groups. These are the chemical groups that can react with the (-OH) groups of the primary resin chains. Such a reaction will result in a connection between the HMMM and the primary chain. Because it contains six (CH₃OCH₂-) groups, the HMMM can attach itself to as many as six different primary chains, and can therefore serve as junction points for the network (see Figure 1). It should be noted that, despite the relative sizes of the molecular drawings in Figure 2, the primary resin chains will typically be much larger than the crosslinking agent molecules.

Chemically, the crosslinking occurs by a condensation reaction which produces methanol (CH₃OH) as a by-product:



This curing reaction requires the presence of a small amount of acid catalyst. You will use *para*-toluene sulfonic acid (*p*-TSA).

Also, elevated temperatures are needed for the reaction to take place. After the components (primary resin, crosslinking agent, catalyst, and some solvent) are applied to a surface as a liquid film, the coated part will be heated in an oven for a specified time. The crosslinking can therefore be controlled and delayed until an appropriate time after application. You may have heard of automobile finishes being "baked" in this fashion.

The degree of crosslinking, and therefore the final properties, of the cured films can be controlled by a number of factors. Two that you will explore are the curing temperature, and the ratio of crosslinking agent to primary resin in the liquid mixture. The degree of crosslinking will generally increase as the cure temperature is increased, because this speeds up the reaction. Also, adding more crosslinking agent to the mixture will, to a point, result in more extensive crosslinking.

Two important coating properties you will measure for these cured films are hardness and impact resistance.

Although there are a number of methods available to measure the hardness of polymeric materials, one of the most fundamental involves attempting to scratch the material with objects of differing hardnesses. This is in fact what you will do in this laboratory, using a series of

pencil leads to evaluate the hardness of your coating. This type of hardness measurement is particularly appropriate for these materials, because coatings in service may have to resist scratching or gouging by hard objects.

You will expose the cured materials to impact by dropping a weight onto coated steel panels. Although other impact tests (Charpy, etc.) are available which can provide controlled rapid deformation of bulk specimens, subjecting the polymers to impact as thin films on substrates better simulates service conditions for these materials, and does not require machining of special sample geometries.

PROCEDURE

Note to Instructor: Many commercially available products can serve as components for the coating mixtures. The procedure as described here, as well as the results shown in the next section, are for a specific experiment which uses the following raw materials (different materials may require slight modifications, as specified by the supplier):

- primary resin—hydroxyl-functional polyester, #57-5803, Cargill, Inc., Minneapolis, MN.
- crosslinking agent (HMMM)—Resimene[®] 747, Monsanto Co., St. Louis, MO.
- acid catalyst (*p*-TSA)—K-Cure[®] 1040, King Industries, Norwalk, CT.

1. ****CAUTION**** This step should be conducted in the fume hood!!

Prepare three different coatings formulations in small jars. The ratio (by weight) of primary resin to crosslinking agent should be varied as follows:

Formulation A- 85:15

Formulation B- 70:30

Formulation C- 55:45

These ratios should be based on the "solids" portion of the components. That is, if the components as supplied contain an added solvent, the solvent fraction is not included in the ratios.

Add solvent (xylene, methyl isoamyl ketone, or other as recommended by resin supplier) to the formulations such that each contains 30% solvent overall. Remember to include in this 30% any solvent that may have been originally contained with the components. At 1% by weight, add to each mixture the K-Cure[®] acid catalyst product. Mix each formulation thoroughly with a mixing stick or spatula.

Note to Instructor: In the interest of time, formulations can be completely or partially mixed for the students in advance, although determining appropriate amounts for each component can provide a good exercise, especially if the compounds originally contain a solvent fraction. When mixed in advance, the formulations may have a limited shelf-life

(several weeks). Also to save time, a shorter experiment can be conducted which examines only one formulation instead of three.

2. ****CAUTION**** This step should be conducted in the fume hood!!

Prepare samples by applying thin films of the coating mixtures to steel panels. Because the measured mechanical properties of a film can be affected by its thickness, it is important that uniform, constant thickness films be prepared for all samples. For each sample preparation:

Place a panel on the glass plate (it can be secured with a small piece of masking tape). Deposit an amount (approximately 1 teaspoon) of the coating mixture near the far end of the panel, in the center of its width. Place the drawdown bar with the 0.15 mm clearance (see Appendix) at the far end of the plate and, in a continuous motion, pull it toward you across the liquid so that it leaves behind a film. It may take a trial or two for practice, but you should soon be able to quickly prepare film samples that appear smooth and uniform. The bar should be cleaned with a quickly evaporating solvent such as acetone between each sample preparation. Make three replicate samples for each combination of formulation type (A, B, or C) and curing temperature you intend to test (remember to label the panels with a marker!). Let each panel sit horizontally for at least ten minutes before curing (step 3) to allow for solvent evaporation.

3. For each test temperature, cure the samples by placing them (3 for each formulation) into the appropriate preheated oven. Panels can be placed horizontally or hung vertically in the oven. Curing temperatures in the range 70 - 190 °C should be investigated—see instructor for specific temperatures and ovens to be used. For each cure temperature, use a baking time of 30 minutes.

Note to Instructor: If time and the number of available ovens make it difficult to examine several different cure temperatures, try instead using a single temperature and varying the amount of time samples remain in the oven. This will also produce films with varying degrees of crosslinking.

4. After the panels are removed from the oven and have cooled, lightly touch the films with your finger. Have they become hard and rigid, or are they still sticky and tacky? Using the micrometer, measure the thickness of the cured films. You can do this by obtaining

the difference in thickness between coated and uncoated portions of the panel. Check for uniformity between samples and within the same sample. Is the final film thickness the same as the clearance of the drawdown bar?

Note to Instructor: The thickness of the cured films will be considerably less than the drawdown bar clearance. The bar will leave behind a wet film that is typically about half as thick as the bar's clearance. This film will then contract upon solvent evaporation and curing. Using a bar with a 0.15 mm clearance depth, we obtained cured films that had thicknesses in the range 0.04 - 0.05 mm.

5. Measure the hardness of the cured films by comparing their hardnesses to those of the pencils. Pencil leads are ranked in order of increasing hardness as follows: •

6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H

In a controlled fashion (see below), you will try to cut into each coating with these pencils. Leads harder than the coating will be able to gouge the film, while those softer than the coating will crumble and will leave the film uncut. For each trial:

Adjust the lead so that approximately 3 mm extends from the lead holder. With the lead holder perpendicular to a piece of abrasive paper, prepare the lead by grinding it against the paper so that a flat surface, normal to the lead's length axis, is obtained. Place the test panel horizontally on a flat surface. With the pencil pointing away from you, place the lead against the film at a 45° angle, and push the lead down and away from you in an attempt to cut the film. An alternative method is to grip the pencil in your fist, and hold the lead against the surface such that it is pointing toward you (45° to the surface), and then pull rather than push the lead. In either case, you must exert enough downward pressure so that either the paint film is gouged (preferably down to the steel panel surface), or the lead crumbles. Make at least three trials with each lead tested, and note whether that lead cuts the film or not. The hardness of the film is reported as that of the hardest lead which does not gouge the film.

Note to Instructor: This procedure can be supplemented by having students read ASTM D3363-74: Film Hardness by Pencil Test.

6. ****CAUTION**** Be certain to wear safety glasses while using this apparatus!!

Using the drop weight tester, investigate the films' resistance to impact. This will provide a measure of their brittleness—a lower impact resistance indicates a more brittle (less tough) material. For each test:

Place the coated panel horizontally on the support ring with the film facing upward. Raise the weighted indenter to a specified height inside the drop tube, and allow it to fall onto the panel. The energy of the blow is given by the load (indenter weight) multiplied by the height from which it was dropped. Joules or inch-pounds are appropriate units for impact energy. Remove the panel, and examine the film in the impact area. A failure is indicated by cracks caused by the blow. A magnifying glass may be useful, although failures are usually detected easily by eye. Note the energy of each impact, and whether a failure occurred.

You are trying to determine the highest impact energy each film can sustain without failure. Perform tests from different heights and try to determine the impact energy at which the film exhibits a transition from passing to failing (i.e., if it passes the first test, you would increase the drop height). You can perform several tests on the same panel as long as a flat, coated area can be placed over the entire support ring. Beginning with large variations, you should be able to locate the transition point to within a drop height of 25 cm. If possible, try to narrow it down to within a 10 cm height, and perform multiple tests from several heights in this region. Report the "impact energy" of the sample as the highest energy at which the sample consistently does not fail.

NOTE: For all samples, use the 0.9 kg indenter initially. If no failure is achieved even from the greatest possible height, switch to the 1.8 kg indenter.

7. (optional) Measure the hardness of the test films using a Knoop indenter on the Tukon® Microhardness Tester. Use an applied load of 50 g. Report hardnesses as Knoop Hardness Numbers (KHN).

EXPERIMENTAL RESULTS

All samples baked at 90 °C and above became hard to the touch after removal from the oven. Samples exposed to a lower curing temperature (70 °C) remained sticky and fluidlike. It can be concluded that little crosslinking occurred at this low temperature, and these films were not subject to the hardness and impact tests.

Figure 3 shows the pencil hardness for all films cured at 90 °C and above. The 55:45 and 70:30 mixtures produced films whose hardness increased from HB to 3H as the curing temperature was raised from 90 to 130 °C. The increase in crosslink density caused by curing at higher temperatures resulted in greater film hardnesses. For these two formulations, the pencil test did not detect any further changes in hardness at cure temperatures above 130 °C.

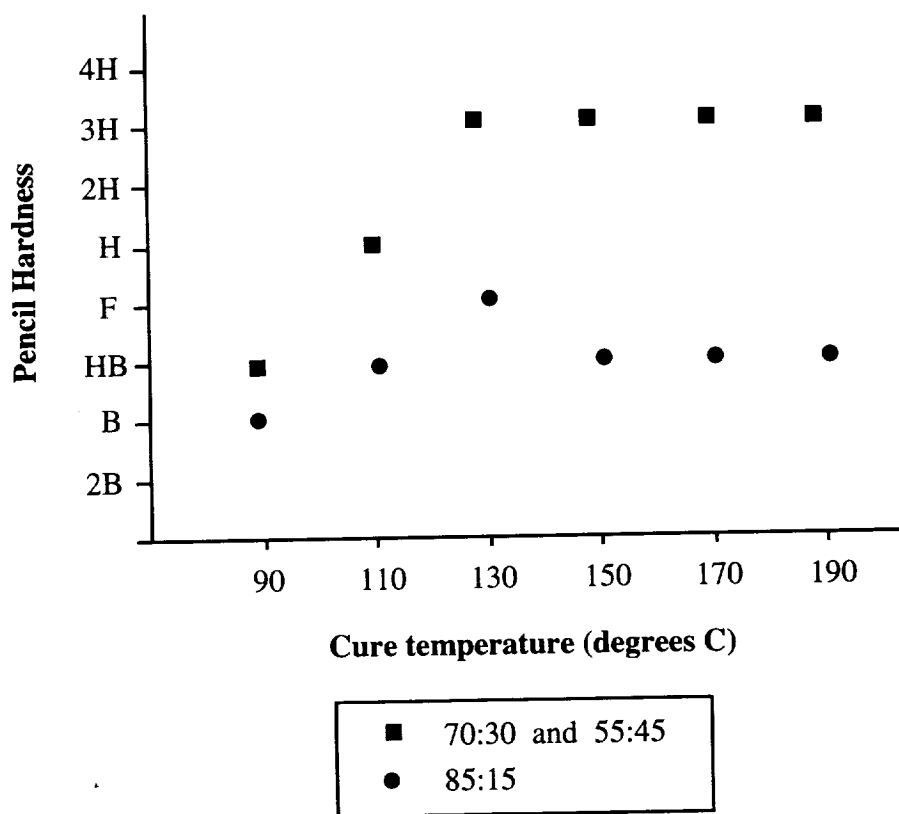


Figure 3. Pencil Hardness Values for Cured Films

Although the pencil hardness results for the 55:45 and 70:30 formulations were indistinguishable, films made from the 85:15 mixture (the one containing the least amount of crosslinking agent) exhibited significantly lower hardnesses at all curing temperatures. While also showing some increase in hardness with temperature, this formulation achieved a maximum hardness of only F. The behavior of the 85:15 samples demonstrates that reducing the amount of crosslinking agent in the mixture can result in significantly softer films.

It is interesting to compare pencil hardness results with Knoop Hardness Numbers (KHN) for these films. KHN values for the series of films from the 70:30 mixture appear in Figure 4. Indentations were measured at least thirty seconds after the Knoop indenter was removed; no changes in the measured indentation were noted at increased times (up to 10 minutes). The general trend of hardness increasing with cure temperature, seen in the pencil hardness results of Figure 3, is confirmed. Because the KHN analysis provides a less discretized measure of hardness, the curve in Figure 4 shows a somewhat smoother increase and leveling of hardness compared to the pencil test. Also note that the Knoop test identifies significant changes in hardness above the 130 °C cure temperature that were not detected in the pencil test. (*Note to Instructor:* Have students comment on the relative merits and drawbacks of the two types of hardness tests.)

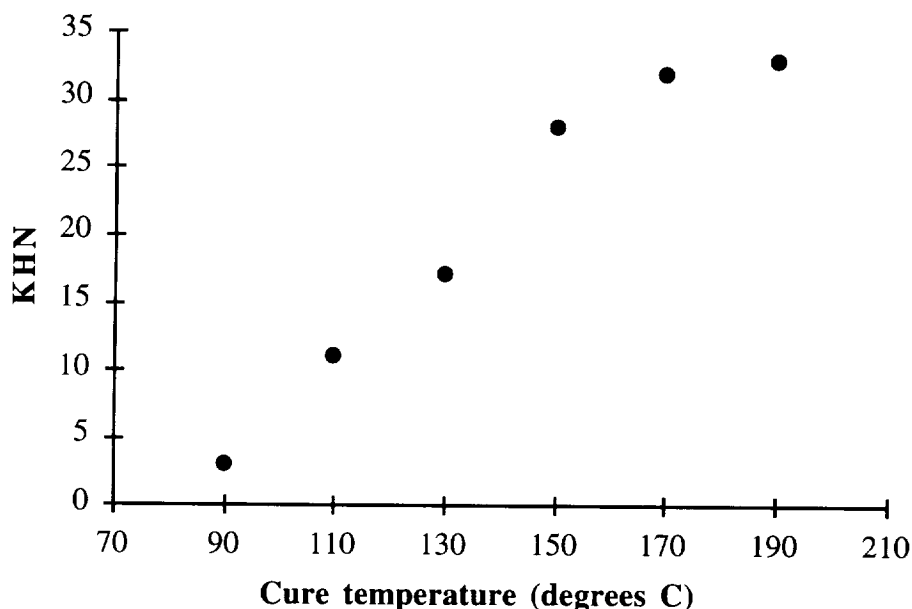


Figure 4. Knoop Hardness Numbers for Cured Films from the 70:30 Formulation

Figure 5 contains impact energy results from the drop weight test. Note that 20 Joules was the highest impact energy that could be achieved experimentally. Samples with a listed impact energy of 20 J did not exhibit any failure through the entire measurement range.

Films from all formulations showed considerable toughness and flexibility at the lowest cure temperatures, showing no failure even under an impact of 20 J. For films made from the 55:45 mixture (the highest crosslinking agent percentage) detectable failures appeared at a cure temperature of 130 °C (impact energy of 16 J). Further increases in the cure temperature for this formulation resulted in increased brittleness—impact energies fell to a final value of 3 J for the 190 °C cure. Similar behavior is seen for films from the 70:30 mixture. The changes these materials exhibit as a function of cure temperature indicate a strong inverse relationship between impact energy and degree of crosslinking.

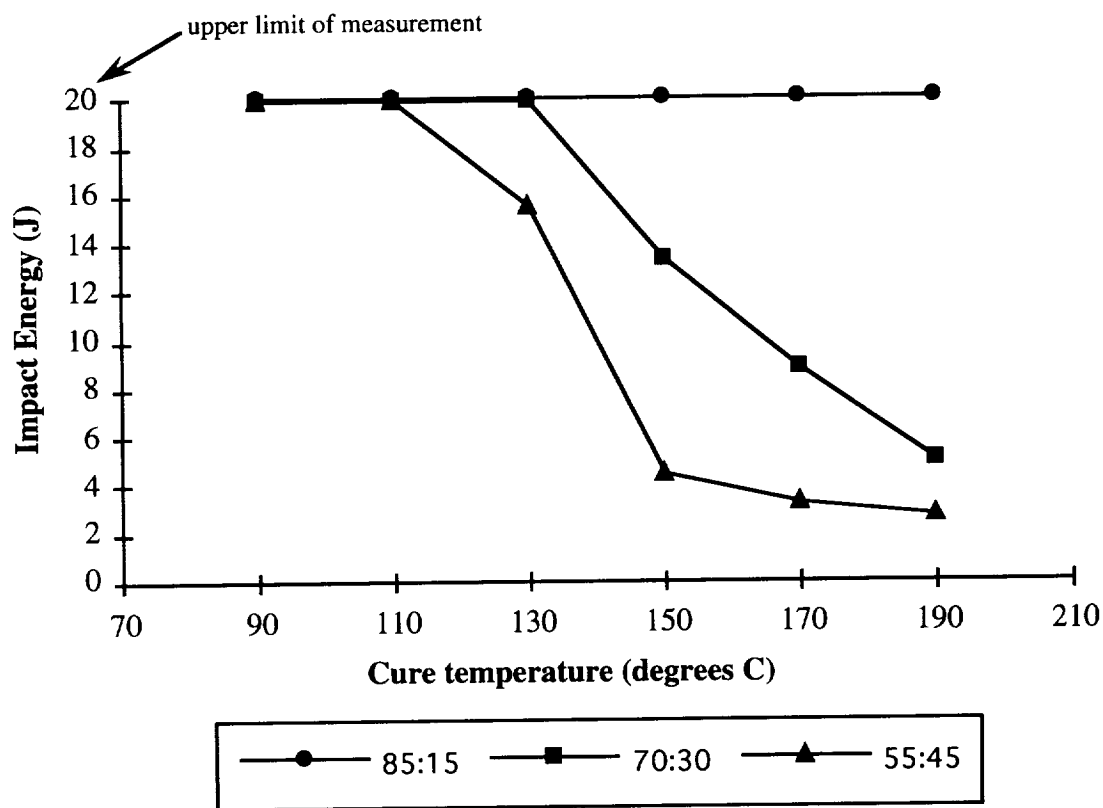


Figure 5. Impact Energies for Cured Films (a value of 20 J indicates no observable failure throughout the entire measurement range)

For cure temperatures where some samples exhibited detectable impact failures, the effect of crosslinking agent ratio on film toughness is apparent. The formulation with the largest percentage of crosslinking agent, 55:45, produced the most brittle films. The 70:30 samples had somewhat higher impact energies, and the 85:15 mixture produced the least brittle films, which did not show impact failures even when cured at 190 °C. This supports the earlier conclusion that more extensive crosslinking in these materials leads to a reduction in impact resistance. Even though samples from the 85:15 mixture are relatively tough, recall that they also exhibited considerably lower hardnesses than those from the other two formulations.

In summary, the hardness and impact energy of these organic coatings are directly related to their internal network polymer structure, in particular, the degree of crosslinking, which can be adjusted by changing the crosslinking agent percentage in the formulation, as well as the film's cure temperature. These materials display a tradeoff between hardness and toughness, with harder films generally exhibiting a lower resistance to impact. For a given application, changes in the formulation and cure temperature can be used to prepare coatings with an optimum combination of these mechanical properties.

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Appendix—Equipment Notes to Instructors

The *drawdown bar* is a steel bar, 3 to 4 inches in length, with a flat side that rests squarely on the test panel. Along this side, a 2-inch long section has been machined away such that it provides a clearance, which will leave behind a film when the bar is drawn along the surface of a panel and over the deposited liquid mixture, as described in the Procedure. We

used a bar with a clearance depth of 0.15 mm (6 mil). Draw down bars are available commercially from Paul N. Gardner Co., Inc., Pompano Beach, FL.

In the *drop weight impact test*, the test panel sits horizontally on a circular steel support ring. A 4-foot long vertical tube, with a slot cut along its length, is positioned directly above the center of the support ring. A cylindrical steel weight, tapered at the impact end to a hemispherical tip, fits inside the tube. A bolt protruding from the side of the indenter weight fits through the slot in the tube, and is used to lift the weight to the desired drop height. A unit conforming to ASTM guidelines can be made by referring to ASTM D-2794-90: Resistance of Organic Coatings to the Effects of Rapid Deformation, although alternate designs would be suitable for the purposes of this experiment. A commercial device of this type is available from Paul N. Gardner Co., Inc. (see above).